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ATOMIC AND MOLECULAR PROCESSES IN  
ATMOSPHERIC ENVIRONMENTS

M. A. Biondi

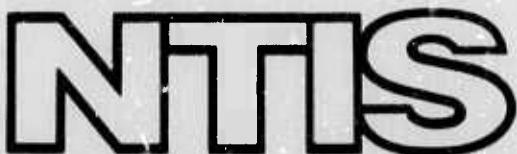
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13. ABSTRACT

This summary presents the most recent progress in the following area:

- (1) Radiative Properties of Simple Molecules and Atoms for Optical Discrimination Studies
- (2) Infrared Emission from Recombination and Energy Transfer Process of Air Species
- (3) Ground Based Observations, Rocket and Satellite Measurements and Aeronomy Calculations
- (4) Model Calculations of Atmospheric Composition and Response

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TECHNICAL PROGRESS REPORT NO. 14

Pittsburgh Atmospheric Sciences Institute

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I. Summary of Research

The following research projects are identified by title, senior investigator(s) in charge of the work, and task designation(s) in the ARPA work statement. This summary only covers advances during the period since our last progress report (dated October 23, 1972).

A. Laboratory Studies

- la. Radiative Properties of Simple Molecules and Atoms for Optical Discrimination Studies (E. C. Zipf)(Tasks a and d).

We are now working actively in the 500 - 1100 $\text{\AA}$  wavelength region measuring the absolute cross sections for the direct and dissociative excitation of O, O<sub>2</sub>, N, and N<sub>2</sub> by electron impact. During this report period we have made preliminary measurements on 36 intense EUV features in this region; some of our results are summarized in Table 1. The cross sections, in general, are quite large and have important geophysical implications as the abstract of a paper, that we recently submitted to the Journal of Geophysical Research, attests:

Comment on the Role of Photoionization in Auroral Arcs.

Very large fluxes of extreme ultraviolet [EUV] radiation have been observed in-situ by Paresce et al (1972) in an otherwise weak auroral display ( $\lambda 5577\text{\AA}$  intensity at 5 kR or less). Their measurements, as well as independent ground-based and rocket observations of the c'  $^1\Sigma_u^+ \rightarrow a^1\Pi_g$  intercombination bands

[Dick, 1970], suggest that the total EUV production rate in an auroral arc is comparable in magnitude to the total  $N_2$  ionization rate. The observation data are shown to be consistent with recent laboratory measurements of the absolute cross sections for exciting EUV radiation by electron impact on atmospheric gases, and with in-situ electron-energy distribution measurements. Below 120 km locally excited EUV photons are readily absorbed and efficiently photoionize the neutral constituents of the auroral arc. Radiation entrapment is important for some of these EUV transitions and the concomitant flux enhancement which occurs within the optically thick medium, increases the net photoionization rate. Because the bulk of the EUV radiation is emitted in the 800 - 1000 $\text{\AA}$  region, preferential photoionization of O,  $O_2$ , and NO occurs. This selective ionization alters the ion chemistry in an auroral arc, changes the  $NO^+/O_2^+$  ratio in a complex manner depending on the local NO abundance, and may explain some of the compositional anomalies observed by mass spectrometers.

The EUV column production rates listed in Table 1 are for a Class I aurora; they are impressively large. We are continuing active work on this problem. These measurements are complicated by severe absolute calibration problems, but we are making good progress in extending the molecular-branching ratio technique to this difficult wavelength region.

We have completed our work on atomic nitrogen in the middle UV. This work will appear shortly in the Journal of Chemical Physics:

Excitation of Atomic Nitrogen by Electron Impact. Absolute cross sections have been measured for the excitation of the

NI( $\lambda\lambda 1134\text{\AA}$ ,  $1164\text{\AA}$ ,  $1168\text{\AA}$ ,  $1200\text{\AA}$ ,  $1243\text{\AA}$ , and  $1743\text{\AA}$ ) multiplets by electron impact on atomic nitrogen. The  $\lambda 1134\text{\AA}$  and  $\lambda 1200\text{\AA}$  cross sections are large, reaching  $1.8 \times 10^{-16} \text{ cm}^2$  and  $2.3 \times 10^{-16} \text{ cm}^2$  at their peaks, respectively. The magnitude of these cross sections is about a factor of two lower than the values reported previously by the authors, due to the discovery of a fault in the apparatus. The presence of vibrationally excited molecular nitrogen in the discharged gas is confirmed, and its effect on the measurements is discussed. The ratio of the oscillator strengths of the  $\lambda 1200\text{\AA}$  and  $\lambda 1134\text{\AA}$  resonance transitions is measured to be  $2.6 \pm 0.3$ . The branching ratio of the NI( $\lambda 1311\text{\AA}/\lambda 1164\text{\AA}$ ) multiplets is measured to be  $.28 \pm 0.3$ . Striking differences in the distribution of intensity between the spectra of atomic nitrogen and molecular nitrogen excited by energetic electrons suggest an optical method for measuring the density of atomic nitrogen in the upper atmosphere.

10. Infrared Emission from Recombination and Energy Transfer Process of Air Species. (F. Kaufman)

The first phase of our studies of infrared chemiluminescence processes has been successfully completed with the measurement of the absolute radiative rate constant of the O + NO emission from 1.2 to 4.0  $\mu\text{m}$ . This spectrally resolved emission can now serve as a secondary standard for the absolute measurement of the infrared glows in the flow systems as long as these glows similarly fill the detector optics and overlap the O + NO spectrum, and as long as O<sub>-</sub> and NO<sub>-</sub> concentrations can be measured by standard techniques. Through calibration which used two black body sources and took account of the geometries of the

Table 1

Molecular EUV Radiation From the Direct Excitation  
of N<sub>2</sub> by Electron Impact

Transition Number	Identification	Wavelength (Å)	Cross Section* (cm <sup>2</sup> )	Column Production Rate + (kR)
1	f → X <sup>1</sup> Σ <sub>g</sub> <sup>+</sup> (6)	1034.8	6.9 (-19) <sup>#</sup>	0.4
2	f → X <sup>1</sup> Σ <sub>g</sub> <sup>+</sup> (5)	1011.8	1.1 (-18)	0.6
3	—	1004	6.6 (-19)	0.4
4	f → X <sup>1</sup> Σ <sub>g</sub> <sup>+</sup> (4)	989.7	1.5 (-18)	0.8
5	c' 1Σ <sub>u</sub> <sup>+</sup> (0) → X <sup>1</sup> Σ <sub>g</sub> <sup>+</sup> (1)	980.3	2.0 (-18)	0.9
6	f → X <sup>1</sup> Σ <sub>g</sub> <sup>+</sup> (3)	968.3	1.5 (-18)	0.8
7	c' 1Σ <sub>u</sub> <sup>+</sup> (0) → X <sup>1</sup> Σ <sub>g</sub> <sup>+</sup> (0)	958.6	1.5 (-17)	7.0
8	f → X <sup>1</sup> Σ <sub>g</sub> <sup>+</sup> (2)	947.4	1.8 (-18)	0.9
9	f → X <sup>1</sup> Σ <sub>g</sub> <sup>+</sup> (1)	927.1	6.5 (-19)	0.4
10	—	918	1.2 (-18)	0.7
11	—	908	1.1 (-18)	0.6
12	h <sup>1</sup> Σ <sub>u</sub> <sup>+</sup> → X <sup>1</sup> Σ <sub>g</sub> <sup>+</sup>	882.3	9.5 (-19)	0.5
13	—	865.3	1.2 (-18)	0.7
14	—	833.2	5.8 (-19)	0.4
		SUM		15

\* Value at 100 eV (Stone and Zipf, 1973 b)

# Read 6.9 × 10<sup>-19</sup> cm<sup>2</sup>

+ Normalized to a λ3914<sup>o</sup> Å intensity of 5 kR

chemiluminescent glow and of the black body by two simple computer programs, the second-order rate constant,  $I_{\lambda}^{\circ}$ , was found to be  $(2.4 \pm 0.1) \times 10^{-17} \text{ cm}^3 \text{ sec}^{-1} \mu\text{m}^{-1}$  at  $\lambda = 1.51\mu\text{m}$ , and, since the emission spectrum had been determined quantitatively, absolute values of  $I_{\lambda}^{\circ} : I_{\lambda}/[NO]$  are now available from  $\lambda = 1.2$  to  $3.3\mu\text{m}$ . Between  $3.3$  and  $4.0\mu\text{m}$  the spectrum is dominated by a band peaking at  $3.7\mu\text{m}$  whose origin appears to be a vibrational combination tone of  $\text{NO}_2$ , probably  $(v_1 + v_3)$ , whose intensity does not scale linearly with  $[NO]$ , and which seems to be pressure dependent. Further work on this band is still in progress. The spectrally integrated rate constant,  $I^{\circ}$ , which Fontijn, Meyer, and Schiff had reported to be  $6.4 \times 10^{-17} \text{ cm}^3 \text{ sec}^{-1}$  at  $295^{\circ}\text{K}$  up to  $\lambda = 1.4\mu\text{m}$ , and Vanpee, Hill, and Kineyko had found to be  $10.9 \times 10^{-17}$  (corrected for temperature) up to  $2\mu\text{m}$ , can now be further adjusted for its infrared component. This places  $I^{\circ}$  between  $9.6$  and  $11.4 \times 10^{-17} \text{ cm}^3 \text{ sec}^{-1}$  out to  $3.3\mu\text{m}$ . A publication describing this work is about to be submitted to the Journal of Chemical Physics.

Absolute measurements of other emissions such as  $\text{O}_3 + \text{NO}$ ,  $\text{N} + \text{O}_2$ ,  $\text{H} + \text{NO}_2$  are about to be studied.

## 2. Clean Air Chemistry and Chemiluminescence (F. Kaufman)(Tasks a and d).

Excellent progress has been made in our kinetic studies of OH reactions using resonance scattering techniques. The reactions include  $\text{OH} + \text{NO}_2 + M \xrightarrow{1} \text{HNO}_3 + M$ ,  $\text{OH} + \text{NO} + M \xrightarrow{2} \text{HNO}_2 + M$ , and  $\text{OH} + \text{O}_3 \xrightarrow{3} \text{HO}_2 + \text{O}_2$ . The first two were investigated for  $M = \text{He}$ , Ar, and  $\text{N}_2$  at pressures of 1 to 10 torr and seem to be substantially at their low pressure (third order) limit. Values of  $k_1^{\text{Ar}} = 1.0 \times 10^{-30}$ ,  $k_1^{\text{N}_2} = 1.8 \times 10^{-30} \text{ cm}^6 \text{ sec}^{-1}$  were found at  $296^{\circ}\text{K}$ .  $k_1^{\text{He}}$  is still under investigation.  $k_2$  is somewhat smaller, i.e.,  $k_2^{\text{He}} = 0.32 \times 10^{-30}$ ,  $k_2^{\text{Ar}} = 0.32 \times 10^{-30}$ , and a tentative

value of  $k_2^N = 0.49 \times 10^{-30}$  can be reported. Both reactions show the expected negative temperature dependences which can be expressed as  $E_1 = 1.8 \text{ kcal mole}^{-1}$ ,  $E_2 = -2.0 \text{ kcal mole}^{-1}$ . A preliminary account of this work was published in Chem. Phys. Letters 16, 375 (1972) and a major paper on reactions 1 and 2 is in preparation.

Reaction 3, which is the principal step in the catalytic destruction of  $O_3$  by  $HO_x$ , was measured directly by mixing OH, made by the H + NO<sub>2</sub> reaction, with O<sub>3</sub> generated in an ozonizer, adsorbed on silica gel at 195°K, and eluted with Ar at about 218°K. At 297°K  $k_3$  was found to be  $(5.5 \pm 1.5) \times 10^{-14} \text{ cm}^3 \text{ sec}^{-1}$  and measurements from 220 to 450°K provided an Arrhenius expression of  $1.3 \times 10^{-12} \exp(-1.9/RT) \text{ cm}^3 \text{ sec}^{-1}$ . A brief account of this study is about to appear in Chem. Phys. Letters.

### 3. Energy Partitioning in Metal Atom Chemi-excitation (M. A. Biondi, and F. Kaufman).

Following publication of our early work on Na excitation by active nitrogen in Chem. Phys. Letters 16, 380 (1972), which had ruled out vibrationally excited N<sub>2</sub> ( $X^1\Sigma_g^+$ ) as the major precursor and had led to a tentative identification of N<sub>2</sub> ( $A^3\Sigma_u^+$ ) as the species responsible for the D-line emission, major modifications of the apparatus were undertaken. The flow system was rebuilt to facilitate quantitative measurements of  $\langle v_j \rangle$  and of  $\langle N_2^* \rangle$  and a new Na oven was designed and built which makes possible the use of highly purified Na provided in glass ampoules. Due to Dr. Gann's departure to take up a position at the Naval Research Laboratory and Dr. Golde's needed concentration on infrared studies described above, experimental work on this problem has been delayed, but will get under way again in the next two months.

### 4. Neutral-Neutral Reactions in Crossed Beams (W. L. Fite)(Tasks a and d).

Three activities have been prominent during the reporting period on this series of experiments.

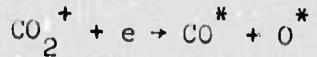
The first is the mathematical analysis of the data on the Ba +  $O_2 \rightarrow BaO + O$  reaction. This work which is the final portion of the PhD thesis of Mr. Bock Kim is progressing well but is not yet completed.

The second activity has been continued experimentation with associative ionization reactions, and particularly preparation for study of the reactions of U with ozone. This is a particularly interesting reaction since energetically one can expect to find both  $UO^+$  and  $UO_2^+$  ions. The manner of the branching between two allowed associative ionization reactions is believed to be capable of illuminating several fundamental points about this class of reactions that lead to ionic products in thermal energy neutral products, which may also be internally excited and capable of infra-red radiation.

The third activity has been initiated with arrival of an automatic data processor and peripheral controller (on-line computer, suitably adapted), which occurred in late March. The personnel who will use this instrument on these experiments have been familiarizing themselves with the equipment and with automatic control and data handling and have begun to write the programs required for the neutral neutral reaction studies. We anticipate that this additional piece of equipment will be of absolutely enormous assistance in the performance of these difficult experiments.

##### 5. Processes Involving Metastable Species (E. C. Zipf)(Tasks c and d).

We continue with our afterglow studies on metastable atoms and molecules of aeronomic importance. At the present moment we have been concentrating on the specific production of the following excited species:  $CO(A^1\Pi)$ ,  $CO(a^3\Pi)$ , and  $O(^1S)$  by the dissociative recombination of  $CO_2^+$  ions



This study is particularly interesting because we have direct evidence (for the first time) of a high degree of vibrational excitation in our  $\text{CO}_2^+$  laboratory plasmas, so that we have an unusual opportunity to study quantitatively the dissociative recombination of vibrationally "hot" ions. Our preliminary results (including complimentary  $\text{O}_2^+$  studies) suggest that previous laboratory studies on terrestrial ions ( $\text{O}_2^+$ ,  $\text{N}_2^+$ ,  $\text{NO}^+$ ) may also have involved vibrationally contaminated plasmas so that the apparent total recombination coefficients measured in these experiments may not be directly applicable in upper atmosphere analyses. Our preliminary results have been accepted for publication in the Journal of Geophysical Research:

The Excitation of the CO Fourth Positive System by the Dissociative Recombination of  $\text{CO}_2^+$  Ions. The Fourth Positive system of  $\text{CO}[\text{A}^1\text{II} \rightarrow \text{X}^1\Sigma]$  has been excited in a static afterglow experiment by the dissociative recombination of  $\text{CO}_2^+$  ions. From combined absolute optical and microwave measurements the specific recombination coefficient for exciting the  $\text{CO}(\text{A} \rightarrow \text{X})$  system was found to be  $(2 \pm 0.5) \times 10^{-8} \text{ cm}^3/\text{sec}$ . This value represents approximately 5% of the total recombination coefficient  $(4.0 \pm 0.5) \times 10^{-7} \text{ cm}^3/\text{sec}$  measured in this experiment, implying that  $\text{CO}_2^+$  dissociative recombination will contribute significantly to the excitation of the CO Fourth Positive system in the martian airglow. Corroborative electron heating experiments showed that the magnitude of the specific recombination coefficient decreased as the electron temperature was increased. Evidence was also found for the presence of vibrationally excited

ions in the  $\text{CO}_2^+$  plasma, a result which indicates that analogous laboratory studies on the dissociative recombination of  $\text{O}_2^+$ ,  $\text{N}_2^+$  and  $\text{NO}^+$  ions may have also involved vibrationally hot plasmas.

6. Ion Molecule Reactions and Excitation Processes in a Fast Flow System (F. Kaufman) (Tasks a and b).

With the completion and publication of the  $\text{O}_2^+$  water cluster work in J. Chem. Phys. 57, 3491 (1972) attention was shifted to the problem of measuring water ion hydration rates. Prior to this the water injection and analysis system was greatly improved. Dual heaters were installed in the liquid water reservoir flask so that temperature variations could be reduced by more than an order of magnitude.

The hygrometer detector head was replaced and the entire flow system was made helium leak tight.

Early experiments on the rate of formation of  $\text{H}_3\text{O}^+\cdot\text{H}_2\text{O}$  in He or  $\text{N}_2$  have shown a reproducible inverse dependence of the rate constant on  $[\text{H}_2\text{O}]$  reminiscent of the behavior of  $\text{O}_2^+$  in  $\text{O}_2$  or  $\text{N}_2$  where other weakly bound cluster ions such as  $\text{O}_4^+$  or  $\text{O}_2^+\cdot\text{N}_2$  provide an alternate path for the formation of the water cluster ion. For  $M = \text{He}$ , such an explanation is untenable in the present case, since it would require the existence of  $\text{H}_3\text{O}^+\cdot\text{He}$  at 300°K which is clearly unlikely. The possibility of interference by He metastables was investigated by adding small amounts of Ar upstream of the  $\text{H}_2\text{O}$  injector, but this led to a decrease of the clustering rate constant without removing the strange inverse  $[\text{H}_2\text{O}]$  dependence. A re-check on mass discrimination in the quadrupole mass filter gave poor constancy of total ion count at high  $[\text{H}_2\text{O}]$  as a function of injector position (reaction time), but this could not explain the observed effect for the parent ion,  $\text{H}_3\text{O}^+$ , if

its initial formation is virtually complete within a very small fraction of the reaction time. The measured rate constants for the  $\text{H}_3\text{O}^+ + \text{H}_2\text{O}$  + He reaction 1 to  $2 \times 10^{-27} \text{ cm}^6 \text{ sec}^{-1}$  as  $(\text{H}_2\text{O})$  is decreased from 2.5 to 0.3 mtorr, is in the correct range. Further experiments will clarify this effect and will be followed by a brief study of the equivalent  $\text{D}_2\text{O}$  reactions.

7. Reactions of Metal Atoms with Ions in Magnetically Confined NO<sup>+</sup> Plasmas (W. L. Fite) (Tasks b and j).

Progress on this program has been minimal during this reporting period due to the fact that Dr. H. H. Lo, who has provided the principal scientific effort on the experiments, has been on leave of absence from the University since the beginning of December. Prior to his going on leave, some additional data were gathered on the reactions between NO<sup>+</sup> and metals, which supported our earlier conclusions on the importance of charge transfer relative to chemical rearrangement collision processes and served to firm up our belief that the problems with the magnetic field shaping appear to be pretty well resolved at this point.

It is expected that Dr. Lo will return to the University in about a month at which time the experiment will be reactivated and brought, we hope, to the point where a definitive paper can be written on reactions between NO<sup>+</sup> and metal atoms.

8. Ion-Molecule Reactions at Elevated Temperatures (M. A. Biondi) (Tasks b and j).

The interest in excited ion-charge transfer lasers has led us to investigate charge transfer processes occurring between several rare

gas ions and mercury vapor. Generally, charge transfer, i.e. a process of the type



tends to be slow at thermal energy if both X and Y are atomic species. In contrast to similar reactions between molecular systems, excess energy released in the reaction is not easily absorbed through internal excitation of one of the collision partners. Electronic excitation of the product ion as a result of the collision can occur only when suitable energy levels exist that are close in energy to the difference of the ionization potentials of X and Y. This condition is more likely to be met in cases where a large number of closely spaced electronic levels exists in the product ion, such as in the ions of heavy metals.

Rate constants or upper limits of the rate constants have been determined for five reactions of rare gas ions with Hg. For this purpose, one of our drift tube apparatuses was connected to a thermally controlled reservoir of mercury which provided a source of mercury vapor. The following rate constants were obtained at 300 K:

Ion	Reactant	Rate Constant
He <sup>+</sup>	Hg	$1.3 \times 10^{-9} \text{ cm}^3/\text{sec}$
Ne <sup>+</sup>	Hg	$< 10^{-12} \text{ cm}^3/\text{sec}$
Ar <sup>+</sup>	Hg	$1.6 \times 10^{-11} \text{ cm}^3/\text{sec}$
Kr <sup>+</sup>	Hg	$8 \times 10^{-12} \text{ cm}^3/\text{sec}$
Xe <sup>+</sup>	Hg	$< 10^{-12} \text{ cm}^3/\text{sec}$

No significant variation of the rate constants was observed when the ion energy was increased to about 1 eV.

The rate constant for  $\text{He}^+$  is about two orders of magnitude larger than those of the other rare gas ions, indicating that an accidental resonance may exist in the case of  $\text{He}^+ + \text{Hg}$ . While a rigorous theory of these processes is no easy task, it appears that the observed behavior can be ascribed to different electron transition probabilities in the curve crossing region of the initial and final potential curves of the collision partners. A preliminary analysis along those lines indicates that the process with  $\text{He}^+$  is indeed strongly favored over those of the other rare gas ions.

9. Time of Flight Experiments (E. C. Ziff) (Tasks b and d).

We continue to investigate the properties of metastable atoms and molecules, and Rydberg states, and to study hot-atom chemistry using translational-energy spectroscopy. During this report period we have made a careful study of the excited fragments produced by the dissociation of  $\text{CH}_4$  and  $\text{NH}_3$  by electron impact. Numerous resonance features have been observed in the time-of-flight spectra that make it possible to identify uniquely the dissociation channels. From an applied point of view these target gases are proving to be very useful sources of kinetically energetic hydrogen atoms in the  $0.1 \rightarrow 200$  eV energy range.

B. Ground Based Observations, Rocket and Satellite Measurements, and Aeronomy Calculations.

10. Optical Interferometer Studies of the Upper Atmosphere (M. A. Biondi) (Tasks g).

The 150 mm aperture Fabry-Perot interferometer has been installed in the Airglow Observatory at Laurel Ridge, Pennsylvania and has undergone preliminary testing and check-out. In initial searches for nightglow chemi-excitation of sodium, no  $\text{Na D}_2$  profiles have been

detected to a (very preliminary) estimated sensitivity of  $\approx 10$  R. The instrument has successfully measured Na D<sub>2</sub> line profiles produced by resonant scattering of sunlight by the atmospheric sodium layer during the "twilight flash".

11. Optical Photometer Studies of Nightglow Ionospheric Modification.  
(M. A. Biondi)(Task g).

Analysis of the ionospheric modification experiment 6300 $\text{\AA}$  photometer data obtained during the June 1972 series of experiments at Platteville, Colorado has continued under our ARPA Institute Program. Excellent maps of the intensity contours of the enhanced 6300 $\text{\AA}$  regions have been obtained at frequent intervals ( $\sim 1$  minute) during the course of the evening of June 15, 1972. The maps cover a  $32^\circ \times 36^\circ$  ( $\sim 160 \times 180$  km) field of view.

After the f<sub>0</sub>F<sub>2</sub> critical frequency passed below the heating transmitter frequency (wave-penetration) the optically enhanced region was observed to move first SE and then sharply E of its previous position directly over the Platteville transmitter. This behavior is not consistent with the results of usual EM ray-tracing for an ionosphere with normal electron concentration gradients.

Evidence for a substantial vertical development (altitudes from 300 to 400 km) in the optically enhanced region was obtained from observation of a "hole" in the enhanced region  $\sim 10^\circ$  south of the previous enhancement maximum four minutes after the transmitter was turned off. This is tentatively explained by radiating atom "fly-away" on ballistic trajectories in the near-vacuum at the inferred 400 km emitting altitude.

12. Measurement of the Ionized and Neutral Constituents of the Atmosphere  
(T. M. Donahue and E. C. Zipf)(Task h).

During this report period we launched two successful sounding rocket experiments that continued our active involvement in airglow and auroral aeronomy. On 11 December 1972 (jointly with the upper atmosphere group at Johns Hopkins University) we launched an Aerobee 170 rocket from the White Sands Missile Range in support of a dual mission: firstly, to provide solar flux data for the JHU experiment on board Apollo 17 and secondly, to continue with our detailed studies of the midlatitude airglow and ionosphere. A complementary Aerobee payload prepared by the University of Colorado completed the complement of rockets, and the mission was quite successful. During February 1973 we returned to Fort Churchill to resume our auroral studies. The rocket was successfully launched into an active x-ray aurora and the payload recovered with minimal damage. The data from both of these shots is currently being analyzed.

We are now in the final stages of calibrating a high-altitude atomic oxygen experiment scheduled for launching on a Javelin rocket from Wallops Island, Va., during the last week of June 1973. A complementary mesospheric experiment employing an optical mass spectrometer is also nearing completion and will be launched in August 1973 from the White Sands Missile Range. We are also preparing two auroral payloads in collaboration with R. A. Young and G. Shephard at York University, Toronto for launching from Fort Churchill during November 1973.

#### C. Model Calculations of Atmospheric Composition and Response

##### 13. Composition of the Mesosphere and Lower Thermosphere (T. M. Donahue) (Task h).

Analysis of OGO-6 data continues - showing large semi-annual variations (factor of 4) in O density near 100 km implying equally large variations in eddy diffusivity. Large meridional wind velocities are

also implied ( $50 \text{ m sec}^{-1}$ ).

Attempt to measure neutral and ion densities in an aurora (Nike Apache, February 1973) failed due to large background signals.

Density of  $\text{H}_2$ ,  $\text{HO}_2$ ,  $\text{H}$ ,  $\text{OH}$  in the stratosphere, mesosphere and lower thermosphere has been calculated.

#### D. Theoretical Studies

##### 14. Semi-Empirical Methods for Estimating Reaction Rates (E. Gerjuoy)(Task e).

(a) Glauber Theory Calculations. As stated in Technical Progress Summary No. 13, our work on Glauber Theory continues to excite wide interest, and has led the British Journal "Reports on Progress in Physics" to invite E. Gerjuoy and Brian Thomas to write a review on Glauber Theory. Preparation of this review now is underway. In addition, Brian Thomas has completed and submitted for publication jointly with (initial Chen, University affiliation)--a Glauber theory calculation on e-He collisions. As explained in Technical Progress Summary No. 13, in so doing we are beginning to demonstrate the practicality of Glauber calculations for collisions involving atoms more complex than hydrogen; Thomas and Chen's final procedures involved quite modest computing times, and the results compare fairly well with experiment, though not as well as in the case of e-H collisions. As soon as time permits, we will go on to e-Li collisions, which now appear to be quite practical, judging from Thomas' and Chen's results for e-He.

E. Gerjuoy has been invited to participate on a panel discussion at the VII International Conference on the Physics of Electronic and Atomic Collisions, Belgrade, July, 1973, to discuss correlation effects in electron-atom collisions. Such correlation effects are precisely what the student (Dave Brockleband), mentioned in Technical Progress

Summary No. 13, has been assigned to compute. Unfortunately, this student's progress has been extremely slow, and appears unlikely that the calculations will be completed in time for the Belgrade Conference. However, E. Gerjuoy probably will participate in the panel discussion nevertheless.

(b) Rotational Excitation Studies. We have continued our studies of the cross sections for rotational excitation of molecules by slow collisions with neutral particles. We have secured a computer code for close coupling calculations of H-H<sub>2</sub> collisions, which can be used to compare the close coupling results with those obtained by other approximations (e.g., the Chase adiabatic method mentioned in Technical Progress Summary No. 13). We also have almost completed an estimate of the previously neglected double scattering contributions to H<sub>2</sub>CO rotational excitation. Moreover, we are examining the possibility that H<sub>2</sub>CO is rotationally excited via Stueckelberg-type nearly resonant collisions with other neutrals; this mechanism--which is very different from the direct excitation mechanisms for H<sub>2</sub>CO rotational excitation previously examined in the literature--has not heretofore been proposed for H<sub>2</sub>CO rotational excitation.

15. Formal Collision Theory (E. Gerjuoy).

(a) Development and Variational Methods. We are very pleased with the progress on our studies of the utility of variational methods; as explained in Technical Progress Summary No. 13, these studies are being carried on in collaboration with Prof. L. Spruch at N.Y.U. Our long review on routine procedures for obtaining variational principles grows longer and longer, and probably will have to be issued as a monograph; either this review or E. Gerjuoy will be finished during the

next six months. The previously mentioned paper on variational identities has appeared, and has evoked considerable interest. A quite new approach to employing variational principles for matrix elements--wherein the auxiliary functions needed in these variational principles are themselves estimated variationally, via a novel generalization of the Rayleigh-Ritz method for estimating bound state energies--is being typed for submission to a journal; along with Gerjuoy, this work will be coauthored by Spruch, Rosenberg and Rau of N.Y.U. Progress also has been made on the development of variational bounds for matrix elements, but this work is not yet ready for publication. Gerjuoy has been invited to organize and chair a panel on new computational methods at an international conference on impact ionization at Royal Holloway College, London, in July following the Belgrade Conference; at this Conference, Gerjuoy expects to review some of these recent new developments in variational principle research.

(b) Theory of Electron Scattering (J. N. Bardsley). Our computer code for applying the complex coordinate method to electron-atom collisions has been generalized and calculations on e-H and e-He collisions are in progress. We have also begun some calculations on potential scattering in order to try to understand the conditions for convergence on the technique.

Studies of electron-alkali collisions have been initiated in cooperation with Dr. R. K. Nesbet. Although the threshold laws for elastic scattering and ionization have been studied extensively in recent years, no careful examination has been made of electron excitation cross sections in which the electrons have energy distributions which fall rapidly with increasing energy, as is found in most atmospheric problems.

One effect of the threshold behaviour which is of particular interest is the appearance of cusps in the elastic scattering cross sections at the energy at which an inelastic process first appears. We analyzed the conditions for the appearance of these cusps, and demonstrated some errors in the interpretation of experimental observations of this phenomenon. Numerical calculations were then carried out which confirmed the analytic results and revealed a clear cusp arising from the  $^1P$  phase shift. This feature supports the suggestion that the photodetachment cross section for negative ions has a similar discontinuity that can be used to measure electron affinities using a laser beam.

Investigations of  $e-h_2^+$  collisions are being initiated, with the aim of calculating the cross sections, for elastic scattering, vibrational excitation and dissociative recombination. Photo-ionization of  $H_2$  may also be studied as part of this program.

16. Pseudopotential Studies of Atoms and Molecules (J. N. Bardsley).

Two sets of calculations of the electron affinities of alkalis have been completed. Comparison of the two results with the experimental values obtained by photodetachment with laser light show that there are correlation errors of  $\sim 0.05$  eV in the calculations. Study of the correlation effects will be initiated shortly.

Calculations of the interaction potentials for  $Li^+ - Li$ ,  $Na^+ - Na$ ,  $K^+ - K$ ,  $Rb^+ - Rb$  and  $Cs^+ - Cs$  have been completed, and two potential curves have been obtained for each system. These calculations allow one to estimate the cross sections for elastic scattering and charge transfer. Similar calculations on the interaction potentials for neutral alkalis are in progress, and comparison with recent laser

absorption measurements will be made.

Our pseudopotential model is being incorporated in the electron scattering code developed by R. K. Nesbet and some preliminary results have been obtained although these results are satisfactory at moderate energies there are some discrepancies at low energies which will be analyzed shortly.

17. Low Energy Atom-Atom Collision Cross Sections (J. N. Bardsley).

The effects of intermediate metastable states on the formation of dimers in rare gases is being investigated. Our provisional conclusion is that these effects are important in argon only at very low temperatures.

18. Auger and X-ray Spectra (J. N. Bardsley).

Many high temperature plasmas contain highly ionized atoms, and analyses of the energy balance and the level of ionization demand a knowledge of the ionization and recombination rates. Auto-ionizing states are of particular current interest and we have calculated the energies of many such states in oxygen and fluorine. From these energy levels we have obtained the spectra of X-ray photons and Auger electrons. Our results are in good agreement with experiment where comparison can be made, and we have explained several puzzling features in the experimental data. It is clear that observation of either X-rays or Auger electrons can be a useful diagnostic tool for hot plasmas.

**II. Publications and Technical Presentations**

**A. Publications**

"Minimum-Variance Method for Potential Scattering", J. N. Bardsley, E. Gerjuoy and C. V. Sukumar, Phys. Rev. A<sub>6</sub>, 1813 (1972).

"Threshold Behaviour of Inelastic Scattering Cross Sections", J. N. Bardsley and R. K. Nesbet, submitted to the Physical Review.

"Auger Spectra of Highly-Ionized Oxygen and Fluorine", B. R. Junker and J. N. Bardsley, submitted to the Physical Review.

"Inner Shell Ionization in Ion-Atom Collisions", J. N. Bardsley, Comments on Atomic and Molecular Physics, 3, 6, p. 173-180 (1972).

"Measurements of Recombination of Electrons with H<sub>3</sub>O<sup>+</sup>·(H<sub>2</sub>O)<sub>n</sub> Series Ions", M. T. Leu, M. A. Biondi, and R. Johnsen, Phys. Rev. L, 292 (1973).

"Twilight and Nighttime Ionospheric Temperatures from Oxygen λ6300 and λ5577 Spectral Line Profiles", W. A. Feibelman, R. D. Hake, Jr., D. P. Sipler and M. A. Biondi, J. Geophys. Res. 77, 1869 (1972).

"Reaction Rates of Uranium Ions and Atoms with O<sub>2</sub> and N<sub>2</sub>", R. Johnsen and M. A. Biondi, J. Chem. Phys. 57, 1975 (1972).

"Mobilities of Uranium and Mercury Ions in Helium", R. Johnsen and M. A. Biondi, J. Chem. Phys. 57, 5292 (1972).

"Measurements of Recombination of Electrons with HCO<sup>+</sup> Ions", M. T. Leu, M. A. Biondi and R. Johnsen, Phys. Rev. (to be published).

"Measurements of Recombination of Electrons with H<sub>3</sub><sup>+</sup> and H<sub>5</sub><sup>+</sup> Ions", M. T. Leu, M. A. Biondi and R. Johnsen, Phys. Rev. (to be published).

"Positive Ion Chemistry of the D & E Region," Radio Science L, 73 (1972).

"The Altitude of the Scattering Layer near the Mesopause over the Summer Poles", T. M. Donahue and B. Guenther, J. Atmos. Sci. (to be published)

"Glauber Form Cross Sections in p-H and e<sup>-</sup>-H Collision I", E. Gerjuoy and B. K. Thomas, J. Math. Phys. 14, 213-218 (1973).

- "Identities Related to Variational Principles", E. Gerjuoy, A. R. P. Rau and Larry Spruch. J. Math. Phys. 13, 1797-1804 (1972).
- "The Minimum Variance Method for Potential Scattering", E. Gerjuoy, J. N. Bardsley and C. V. Sukumar, Phys. Rev. A, 6, 1813-1818 (1972).
- "Time-Reversal Invariance in the Impact Parameter Method", E. Gerjuoy, J. Macek and R. Shakeshaft, to be published in J. Phys. B.
- "Properties of Resonance Wave Functions", E. Gerjuoy, and R. More, to be published in Phys. Rev. A.
- "Constructing Variational Principal", E. Gerjuoy, A. R. P. Rau, and Larry Spruch, submitted for publication in Phys. Rev. Letters.
- "Detailed Balance as a Check on Impact Parameter Method", E. Gerjuoy and Hsiang Tai, submitted for publication in J. Phys. B.
- "A Useful Extremum Principle for the Variational Calculation of Matrix Elements", E. Gerjuoy, A. R. P. Rau, L. Rosenberg and Larry Spruch, submitted to Phys. Rev.
- "Rates of Multiphotodetachment of Negative Ions", F. H. M. Faisal, J. Phys. B. 5, L258-L261 (1972).
- "Bound-free Transitions in Electromagnetic Field of Arbitrary Intensity", F. H. M. Faisal and N. K. Rahman, J. Phys. B. 6, 559-561 (1973).
- "Multiphoton Excitation in Vibrational-Rotational States of Diatomic Molecules in an Intense Electromagnetic Field", F. H. M. Faisal and N. K. Rahman, Il. Nuovo Cimento, 13B, 114-120 (1973).
- "The Glauber  $e^- + He$  Elastic Scattering Amplitude: A Useful Integral Representation", B. K. Thomas, and F. T. Chen, has been accepted for publication in Phys. Rev. A.
- "Interferometric Study of the Chemiluminescent Excitation of Sodium by Active Nitrogen, R. Gann, F. Kaufman and M. A. Biondi, Chem. Phys. Letters 16, 380 (1972).

"Kinetics of the Reaction  $\text{OH} + \text{NO}_2 + \text{M} \rightarrow \text{HNO}_3 + \text{M}'$ ", J. G. Anderson and F. Kaufman, Chem. Phys. Letters 16, 375 (1972).

"The Air Afterglow Revisited", F. Kaufman, Plenum Press, in publication.

"Kinetics of the Reaction  $\text{OH}(v=0) + \text{O}_3 \rightarrow \text{HO}_2 + \text{O}_2$ ", J. G. Anderson and F. Kaufman, Chem. Phys. Letters, to be published.

"Absolute Rate Constant for the  $\text{O} + \text{NO}$  Chemiluminescence in the Near Infrared," M. F. Golde, A. E. Roche and F. Kaufman, J. Chem. Phys., to be submitted.

"The Dayglow ( $\text{OI}$ )  $\lambda\lambda$  6300 and 5577 Å Lines in the Early Morning Ionosphere", R. A. Schaeffer, P. D. Feldman and E. C. Zipf, J. Geophys. Res., 77, 6828 (1972).

"Excitation of Atomic Nitrogen by Electron Impact", E. J. Stone and E. C. Zipf, J. Chem. Phys., May 1973 issue.

"Emission Line-Shapes Produced by Electron Impact Dissociative Excitation of Atmospheric Gases", W. C. Wells and E. C. Zipf, Trans. AGU, 53, 1068 (1972).

"Excitation of  $\text{CO}(\text{A}^1\text{II})$  Molecules by the Dissociative Recombination of  $\text{CO}_2^+$  Ions", R. A. Gutcheck and E. C. Zipf, Trans. AGU, 53, 1075 (1972).

"Comment on the Role of Photoionization in Auroral Arcs", E. C. Zipf, submitted to J. Geophys. Res., 1973.

"Excitation of the  $\text{OI}(^3\text{S}^0)$  and  $\text{OI}(^5\text{S}^0)$  States by Electron Impact on Atomic Oxygen", E. J. Stone and E. C. Zipf, submitted to J. Chem. Phys., 1973

"The Excitation of the CO Fourth Positive System by the Dissociative Recombination of  $\text{CO}_2^+$  Ions", R. A. Gutcheck and E. C. Zipf, accepted for publication by the J. Geophys. Res., 1973.

B. Technical Presentations

J. N. Bardsley presented four seminars at the IBM Laboratory, San Jose, California in October 1972, entitled

- 1) The Significance of Resonant States
- 2) The Calculation of Resonant States
- 3) Diatomic Potential Curves and Atom-Atom Collisions
- 4) Pseudo-potentials in Atomic and Molecular Physics

"Anti-atomic Physics", J. N. Bardsley, invited paper to the American Physical Society, San Diego, December 1972.

"Twilight Na D<sub>2</sub> 5890Å Spectral Line Profile Produced by Resonant Scattering of Sunlight", M. A. Stoenescu and M. A. Biondi, presented at Fall Annual Meeting of AGU.

"Processes Leading to Recombination Between Charged Particles in Ionized Gases", Seminar on Gas Breakdown and Its Fundamental Processes, October 3 - 6, 1973, Tokyo, Japan.

"Seasonal and Hemispherical Variation of Atomic Oxygen Densities in Lower Thermosphere", T. M. Donahue and R. J. Thomas, presented at Fall Annual Meeting, AGU, San Francisco.

"Exploration of the Outer Planets", Physics Department Student Seminar, University of Pittsburgh.

"Venus, Partly Unveiled", T. M. Donahue, invited paper presented at the Venus I Session of the DPS Meeting, Tucson, March 1973.

"The Mysteries of Venus", address presented at annual meeting of the AAAS, Washington, D. C., December 29, 1973.

"The Achievement of the Space Programs in Planetary Exploration", testimony before Science and Astronautics Committee, H. R., March 16, 1973.

"NO in Auroras", Seminar, Harvard University, March 9, 1973

W. L. Fite attended the Fourth Annual Meeting of the Division of Electron and Atomic Physics, November 29 - 1, December, 1973, Menlo Park, California.

W. L. Fite attended the First Decade of the Coral Gables Conferences on Fundamental Interactions, Coral Gables, Florida, January 22 - 26, 1973.

W. L. Fite gave a departmental colloquium at the University of Windsor, London, Ontario, January 10, 1973.

W. L. Fite gave a departmental colloquium at Yale University, April 4, 1973.

W. L. Fite attended the DNA Symposium on the Physics and Chemistry of the Atmosphere in San Diego, California, April 9 - 12, 1973.

W. L. Fite gave a seminar at Bell Laboratories, Murray Hill, New Jersey, April 18, 1973.

W. L. Fite attended and presented a paper at the American Physical Society Meeting, Washington, D. C., April 23 - 26, 1973.

W. L. Fite gave an invited paper at the Conference of the Division of Atomic and Molecular Physics of the Canadian Association of Physicists, University of Windsor, London Ontario, April 27 - 28, 1973.

"Use of the Glauber Theory in Atomic Collisions", Seminar at the Argonne National Laboratory, Argonne, Illinois, June 30, 1972.

"New Results on Applications of Glauber Theory to Atomic Collisions", invited paper, Third International Conference on Atomic Collisions, E. Gerjuoy, August 7 - 11, 1972, University of Colorado, Boulder, Colorado.

"Use of the Glauber Approximation in Atomic Collision", E. Gerjuoy, at the Division of Electron and Atomic Physics Meeting, San Francisco California, November 28 - December 2, 1972.

"The Air Afterglow Revisited," F. Kaufman, invited paper at Second International Conference on Chemiluminescence, University of Georgia, Athens, Georgia, October 10 - 13, 1972.

"Gas Phase Hydrogen Atom Recombination," F. Kaufman, seminars presented at Air Force Cambridge Research Laboratories, Bedford, Mass., January 19, 1973; at M.I.T., Cambridge, Mass., February 6, 1973; at University of Chicago, Chicago, Ill., February 7, 1973; at Brandeis University, Waltham, Mass., March 1, 1973.

"Some O- and OH- Reactions of Stratospheric Interest", F. Kaufman, seminar presented at Illinois Institute of Technology, Chicago, Illinois, February 8, 1973; at University of Rochester, February 28, 1973; at Harvard University, Cambridge, Mass., March 29, 1973.

"Some Ion-Molecule Reactions Involving Water Vapor," F. Kaufman, seminar presented at Brookhaven National Laboratory, Upton, N. Y., March 14, 1973.

"Lectures on Chemical Reaction Kinetics", F. Kaufman, at the Center for Earth and Planetary Physics, Harvard University, Cambridge, Mass., February 5, 12, 26 and March 5, 1973.

"Emission Line-Shapes Produced by Electron Impact Dissociative Excitation of Atmospheric Gases", paper presented at the San Francisco Meeting of the AGU, December 1972.

"Excitation of CO( $A^1_{II}$ ) Molecules by the Dissociative Recombination of  $CO_2^+$  Ions", paper presented at the San Francisco meeting of the AGU, December 1972.

C. Other Activities Relating to ARPA

M. A. Biondi attended the Ivory Coast Meeting at I.D.A., March 20 - 21, 1973 and presented the paper "Observations of the Optically Enhanced Regions at Arecibo and at Platteville", by D. Sipler, E. Enemark, and M. A. Biondi.

M. A. Biondi and D. P. Sipler participated in the Prairie Smoke IV B series of experiments in Colorado during the period, December 1972 - February 1973.

F. Kaufman attended a meeting on V.U.V. radiation effects at the Institute for Defense Analyses, Arlington, Va. in December 1972.

F. Kaufman attended a review meeting on infrared chemiluminescence at Wayne State University, Detroit, Mich., March 16, 1973.

E. C. Zipf launched a Nike-Apache rocket into a class II<sup>+</sup> auroral arc above Fort Churchill on 1 March 1973.

E. C. Zipf attended the final planning meetings in preparation for the launch of a Javelin (8.61 UA) and bulbous Nike Apache (14.512 UA) rocket this summer from Wallops Island, Va., and White Sands, N.M., respectively.

E. C. Zipf attended a design review meeting for a joint Canadian-American auroral program which will involve the launch of two Black Bryant 5 rockets from Fort Churchill next November.

E. C. Zipf participated in the launch of an Aerobee 170 from the White Sands Missile Range on December 11, 1972. This rocket was launched in support of Apollo 17 and as a continuation of our mid-latitude airglow and ionospheric studies.

#### D. Other Activities

J. N. Bardsley attended the annual meeting of the Division of Electron and Atomic Physics of the American Physical Society, at Menlo Park, California, in December 1972.

J. N. Bardsley participated in the Coral Gables Conference on Fundamental Interactions at the University of Miami, Florida in January 1973.

E. Gerjuoy participated in the Coral Gables Conference on Fundamental Interactions at the University of Miami, Florida in January 1973.

E. Gerjucy meeting regularly with Prof. L. Spruch of N.Y.U. to collaborate on research on Variational Principles.

F. Kaufman was on Sabbatical leave at Harvard University, January through March 1973.

F. Kaufman was elected Vice Chairman of the Division of Chemical Physics, American Physical Society.

F. Kaufman accepted an invitation to organize a Colloquium on Elementary Reactions for the XVth International Combustion Symposium, Tokyo, Japan August 1974.

F. Kaufman attended meetings of the Climatic Impact Committee of the National Academy of Sciences in Washington, D. C. on October 28 and 29, 1972, December 8 and 9, 1972, and March 19 and 20, 1973.

F. Kaufman attended the Second Conference of the Department of Transportation Climatic Impact Assessment Program in Cambridge, Mass. on November 14 - 16, 1972.

### III. Visiting Scientists

S. P. Anand, University of Toronto

Mr. M. Andriolo, Atomika Technische Physik, Munich

A. I. Clark, Canadian Treasury Board

A. C. Colb, Maxwell Laboratories

J. C. Fletcher, National Aeronautics & Space Administration

H. Forsen, University of Wisconsin

T. M. Grabel, Bell Laboratories

D. L. Jauncey, Cornell University

A. Lifshitz, Hebrew University of Jerusalem, Israel

D. C. Morton, Princeton University

T. M. Sugden, Shell Thornton Centre, Chester, England

Degrees Awarded

Mrs. Nancy Poeth, M.S., 1972

<u>Senior Investigator</u>	<u>Est. Funds Expended and Committed (Thousands)</u>
J. N. Bardsley	69.7
M. A. Riondi	370.7
T. M. Donahue	330.1
W. L. Fite	346.9
E. Gerjuoy	327.0
F. Kaufman	346.9
E. C. Zipf	315.2
Total Expended and Committed	2,106.5
Available Funds	<u>2,245.8</u>
Estimated Remaining Funds as of 4/1/73	<u>139.3</u>

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University Accounting of Funds

Expended as of 3/31/73	2,090.2
Available Funds	<u>2,245.8</u>
Remaining Funds as of 4/1/73	<u>155.6</u>